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TITLE: Materials Research Society Symposium Proceedings; Volume 720. Materials Issues for Tunable RF and Microwave Devices III Held in San Francisco, California on April 2-3, 2002

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Dielectric and Room Temperature Tunable Properties of Mg-doped $Ba_{0.96}Ca_{0.04}Ti_{0.84}Zr_{0.16}O_3$ Thin Films on Pt/MgO

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ABSTRACT

Mg- doped $Ba_{0.96}Ca_{0.04}Ti_{0.84}Zr_{0.16}O_3$ (BCTZ) thin films were fabricated on Pt/MgO substrate by metallorganic decomposition method. The structure of the films were analyzed by x-ray diffraction. The electrical measurements were performed on metal-ferroelectric-metal capacitors with platinum as the top and bottom electrode. The dielectric properties were improved after the capacitors were post annealed at 700 °C in oxygen atmosphere for 30 min. A high dielectric constant of 504 and a dissipation factor of less than 4% was obtained at 1 MHz. The Pt/BCTZ/Pt/MgO capacitors exhibited high tunability of 55% at an applied field of 55 kV/cm.

INTRODUCTION

Thin films of barium strontium titanates $Ba_{1-x}Sr_xTiO_3$ have become very attractive as dielectrics for storage capacitors for high density dynamic random access memories(DRAM), decoupling capacitors and electric field tunable elements for high frequency microwave circuits[1-5]. Barium Titanium Zirconate $Ba(Ti,Zr)O_3$, which is a solid solution of barium titanate $BaTiO_3$ and barium zirconate $BaZrO_3$ shows a lot of analogies to $BaSrTiO_3$ solution[6]. $Ba_{1-x}Ca_xTi_{1-y}Zr_yO_3$ (BCTZ) bulk ceramics used as dielectrics for chip capacitors, when prepared in oxidizing atmophere exhibit a broad dielectric constant-temperature (ε-T) curve near the critical temperature T_c, where peak values of $\varepsilon = 18000$ with nickel electrodes have been reported[7]. Since the dielectric constant of BCTZ is significantly higher than that of bulk BST, it was suggested to explore the possibility of using BCTZ thin film as a replacement for BST. The fabrication of doped and undoped BCTZ films on $Pt/Ti/SiO_2/Si$ substrates by metalorganic decomposition (MOD) method and its dielectric properties have been reported by our group recently [8]. The tunability of high dielectric constant materials is an important factor for the fabrication of jitter free high frequency voltage controlled oscillators, matching networks and phase delay elements. So far most of the tunability investigations are confined to BST and strontium titanate thin films. In this paper, we are reporting on the results of electrical characteristics and tunability of magnesium(Mg) doped BCTZ films on Pt/MgO substrates.

SAMPLE PREPARATION

Platinum film of thickness 200 nm was deposited on (100) MgO substrate by DC sputtering. The MOD BCTZ film was deposited by spin on techniques. The details of the preparation of MOD BCTZ is described in our earlier publication [8]. After baking the films at 150 °C for 2 mins and 250 °C for 4 mins the films were annealed at a temperature of 600-900 °C for one hour in flowing oxygen ambient. The thickness of the MgO film deposited was about 180 nm and it was determined using an isoscope. The microstructure of the thin films was characterized by x-ray diffraction.

A top platinum electrode was also deposited by DC sputtering. The capacitor structures of diameter in the range 50 microns to 160 microns were defined by standard photolithography. The top electrode patterned structures were etched by ion milling After the removal of photoresist by plasma ashing, some of the samples were post annealed in oxygen environment for half an hour . Figure 1 shows the cross-sectional structure of the device fabricated. The capacitance – voltage (C-V) characteristics of the metal-ferroelectric-metal structures were determined by Hewlett-Packard HP 4275A multi-frequency LCR meter. The leakage current in the samples were obtained by Hewlett-Packard HP 4145A semiconductor parameter analyzer.

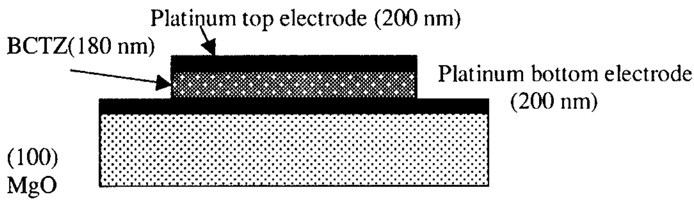

Figure 1. Structure of the fabricated sample.

RESULTS AND DISCUSSION

Figure 2 shows the x-ray diffraction(XRD) spectrum of platinum film on MgO which confirms the formation of (111)Pt film on MgO. In addition, JCPDS based analysis show peaks corresponding to Pt_3O_4 and (100) MgO. Figure 3 shows the XRD pattern of the Mg-doped BCTZ films annealed in the temperature range of 600- 900 °C for one hour in an oxygen environment on the Pt/MgO substrate. The XRD pattern is similar to the XRD pattern of BCTZ films on Pt/Ti/SiO_2/Si substrate which we reported in our previous publication confirming the formation of perovskite phase[9,10]. With increasing annealing temperature from 600 °C to 900 °C the XRD peaks became sharper indicating better crystallinity and an increase in grain size . The grain size for films annealed at 900 °C was less than 100 nm in diameter as determined by Scherrer formula shown below:

$$t = C\lambda/B\cos\theta$$

where C is a factor (typically 0.9 to 1.0), B is the full width at half maximum, θ is the Bragg angle and λ is the x-ray wavelength.

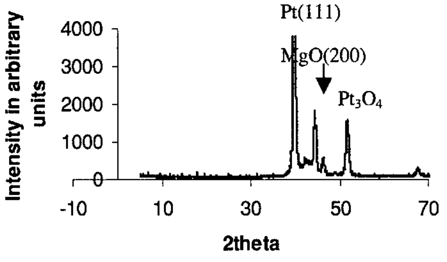

Figure 2. XRD patterns of Platinum film deposited on MgO.

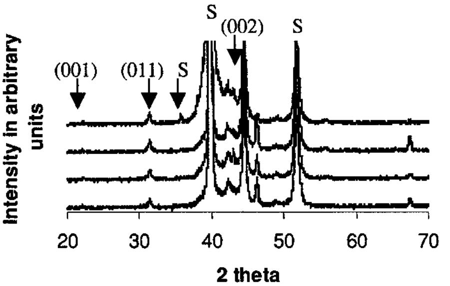

Figure 3. XRD patterns of BCTZ on Pt/MgO annealed at temperatures 600-900°C for one hour. (S: Substrate)

Figure 4 shows the capacitance versus voltage (C-V) characteristics of the Mg doped BCTZ thin film capacitors on MgO measured at a temperature of 300 K and at 1 MHz with an ac signal of 100 mV. The zero bias dielectric constant increased from 105 to 420 for annealing temperatures from 600 °C to 900 °C . The C-V measurements performed on Pt/BCTZ/Pt/Ti/SiO_2/Si showed dielectric constant of 350 at 900 °C annealing temperature. The increase in dielectric constant on MgO substrate may be due to better cystallanity, less interface stress and reduced inter-diffusion between the substrate and the film[11]. In the case of sputtered Pt/Ti on SiO_2/Si substrates, it was found that temperature cycling the films from room temperature to 800 °C in oxygen resulted in increase in tensile stress by 1200 MPa [12,13]. Although such temperature cycling

details are not available for Pt films on (100) MgO, the lattice mismatch between MgO and Pt is about 7.4% at room temperature.

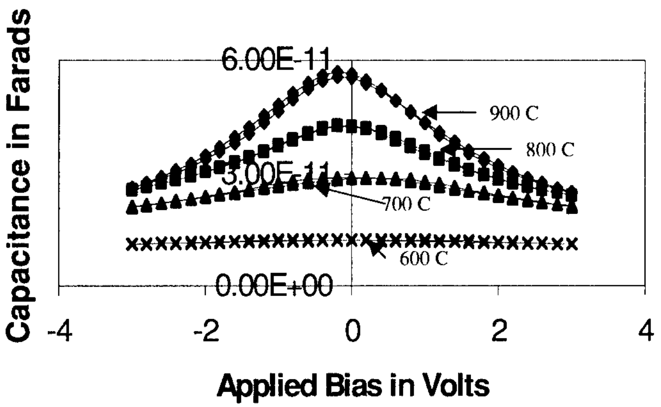

Figure 4. Capacitance vs voltage characteristics of BCTZ film on Pt/MgO annealed in the temperature range of 600-900 °C.

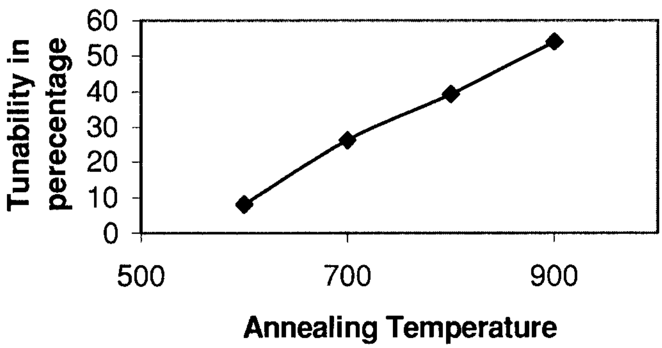

Figure 5. Variation of tunability with annealing temperature for BCTZ films on Pt/MgO.

The BCTZ films annealed at a temperature of 900 °C were post annealed at a temperature of 700 °C in oxygen environment for half an hour. The zero bias dielectric constant(ε) was found to increase from 420 to 504 due to post annealing in oxygen environment and this increase is about 20%. The dissipation factor tanδ for these films were found to be less than 0.04 at a measurement frequency of 1 MHz. The increase in dielectric constant is similar to one reported for Pt/Mg doped BCTZ /$Pt/Ti/SiO_2/Si$ structure post annealed in oxygen environment [14,15]. The increase in dielectric constant due to post annealing in oxygen was attributed to removal of defects which were created during the deposition and patterning of top electrode. The patterning of top electrodes involves standard photolithographic technique using negative resist, ion milling, and plasma ashing. The dielectric constant, ε for the Mg-doped BCTZ film on Pt/MgO is significantly higher than those reported for BCTZ on $Pt/Ti/SiO_2/Si$, $BaTi_{0.88}Zr_{0.12}O_3$ and $Ba_{0.5}Sr_{0.5}TiO_3$ thin films [8,16-18].

The tunability of the capacitance was measured in terms of the parameter $\Delta C/C_o$ where ΔC is the change in capacitance relative to the zero bias capacitance,C_o. The capacitance was measured at 1 MHz frequency with an ac small signal voltage of 100 mV. Figure 5 shows the dependence of tunability for an applied electric field of 55 kV/cm with the annealing temperature. With increase in annealing temperature from 600 °C to 900 °C, the tunability was found to increase from 8% to 55%. The tunability for BCTZ for an applied field of 55 kV/cm is significantly higher than that reported for Mg doped $Ba_{0.6}Sr_{0.4}TiO_3$ film[3]. Therefore, BCTZ is a better alternative for tunable capacitor applications.

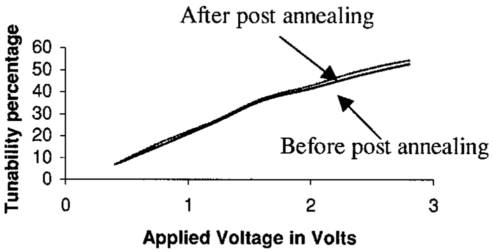

Figure 6. Variation of tunability with applied DC bias voltage.

Figure 6 shows the variation of tunability with bias voltage for sample annealed at a temperature of 900 °C for one hour. The tunability increases linearly with increase of applied voltage from zero volts to 1.6 volts. Further increase in applied voltage resulted in reduced increase in tunability. Figure 6 also shows that the post annealing of samples

in oxygen environment at 700 °C did not show any significant increase in tunabilty with applied voltage.

CONCLUSION

Mg-doped BCTZ thin film was fabricated on a Pt/MgO substrate by metallorganic decomposition method. The electrical characterization of BCTZ film on Pt/MgO shows about 20% higher dielectric constant than films on Pt/Ti/SiO_2/Si substrates. The BCTZ capacitors annealed at 900 °C shows excellent tunability (about 55%) for an applied field of 55 kV/cm. Therefore, BCTZ might be a promising high dielectric constant material for the fabrication of tunable devices.

REFERENCES

1. A. I. Kingon, S. K. Streifer, C. Basceri, and S. R. Sommerfelt, Mat. Res. Bull.,21, 18 (1995).
2. K. R. Caroll, J. M. Pond, D. B. Christey, J. S. Horwitz and R. E. Leuchner. Appl. Phys. Lett., 62, 1845 (1993).
3. P. C. Joshi and M. W. Cole, Appl. Phys. Lett., 77, 289 (2000).
4. C.L. Chen, H.H. Feng, Z. Zhang, A. Brazdeikis, Z.J. Huang, W.K. Chu, C.W. Chu, F.A. Miranda, F.W. Van Keuls and R.R. Romanofsky, Appl Phys. Lett, 75, 412 (1999).
5. J. Im, O. Auciello, P.K. Baumann, and S.K. Striffer, Appl. Phys. Lett., 76, 625 (2000).
6. S. Hoffman and R.M. Waser, Integr. Ferroelectrics, 17, 141(1997).
7. P. Hansen, D. Henning and H. Schreinemacher, J. Am. Cearm. Soc. 81, 1369 (1998).
8. W .-C. Yi, T.S. Kalkur, E. Philofsky, and L. Kammerdiner, Appl. Phys. Lett., 78, 3517 (2001).
9. Powder Diffraction File (International Center for Diffraction Data, Swarthmore, PA, 1995) JCPDS card 36-19.
10. R. Thomas, D.C. Dube, M.N. Kamalasanan, and S. Chandra, Thin Solid Films, 346, 212 (1999).
11. P. Padmini, T.R. Taylor, M.J. Lefevre, A.S. Nagra, R.A. York and J.S. Speck, Appl. Phys. Lett, 75, 3186 (1999).
12. C. Ang, Z. Yu, and L.E. Cross, Appl. Phys. Lett, 62, 228 (2000).
13. G. Schindler, W. Hartner, V. Joshi, N. Solayappn, G. Derbenwick and C. Nazure, Integrated Ferroelectrics, 17, 421 (1997).
14. J. Narayan, P. Tiwari, K. Jagannadham and O.W. Holland, Appl. Phys.lett., 64, 2093 (1994).
15. Y. Shimakawa and Y. Kubo, Appl. Phys. Lett., 77,2590 (2000).
16. T.B.Wu, C.M. Wu, and M.L. Chen, Thin Solid Films, 334, 77 (1998).
17. H.J. Shy and T.B. Wu, Jpn. J. Appl. Phys. Part 1 37, 4049 (1998).
18. D.Wu, A. Li, H. Ling, X.Yin, C. Ge, M. Wang and N. Ming, Appl. Surf. Sci., 165, 309 (2000).